PROCESS MONITORING OF CO_2 ABSORPTION IN DIETHANOLAMINE USING FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

NORHASHIMA BINTI MOKHTAR

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LIST OF ABBREVIATION

ATR	Attenuated Total Reflectance
CO_2	Carbon dioxide
DEA	Diethanolamine
$DEACOO^-$	Carbamate
FTIR	Fourier Transform Infrared Spectroscopy
H_2O	Water
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MSPC	Multivariate Statistical Process Control
PCs	Principal Component
PCA	Principal Component Analysis
PLS	Partial Least Squares
SNR	Signal noise-to-noise ratio

LIST OF SYMBOLS

%	Percentage
λ	Latent
atm	Atmospheric
ml	Mililiter
M	Molarity
ppmv	Part Per Million By Volume
p	Loading Vector
t	Score Vector
t	Time
X	Matrix

PROSES PEMANTAUAN PENYERAPAN CO_2 DALAM DIETHANOLAMIN MENGGUNAKAN SPEKTROSKOPI INFRAMERAH TRANSFORMASI FOURIER (FTIR)

ABSTRAK

Penyelidikan ini adalah tentang pemantauan penyerapan proses karbon dioksida (CO_2) dalam larutan alkanolamin, Diethanolamin (DEA) oleh Spektroskopi Inframerah Transformasi Fourier (FTIR). Ia adalah penting untuk menangkap gas CO_2 dari gas serombong untuk mengurangkan pelepasan gas dalam atmosfera. Hari ini, penyerapan CO_2 oleh pelbagai jenis larutan alkanolamin adalah salah satu proses dominan perindustrian untuk menyelesaikan peningkatan pelepasan gas rumah hijau. Dalam kajian ini, DEA digunakan sebagai penyerap dalam penyerapan CO_2. Objektif utama kajian ini adalah untuk mendapatkan spektrum FTIR bagi sistem CO_2-DEA pada kepekatan dan kadar aliran CO_2 yang berbeza. Kepekatan DEA adalah 2M, 4M dan 6M. Kadar aliran CO_2 adalah 100 dan 200 ml/min. Eksperimen telah dijalankan pada kelajuan pengacau yang tetap, 120rpm. Objektif kedua kajian ini adalah untuk mensintesis spektrum FTIR untuk mencirikan sistem menggunakan Analisis Komponen Utama (PCA). Eksperimen telah dijalankan dengan mengambil sampel bagi setiap 1, 2, 3, 4, 5, 6 dan 7 jam selepas penambahan CO_2 dalam DEA. Sampel dianalisis menggunakan FTIR. Sebagai kesimpulan, Spektra FTIR bagi sistem CO_2-DEA berjaya diperolehi. FTIR sesuai untuk digunakan bagi memantau proses penyerapan CO_2 dalam kepekatan DEA dan kadar alir CO_2 yang berbeza kerana ia memberi analisis yang cepat dan pengukuran yang boleh dipercayai. Teknik PCA boleh digunakan untuk mencirikan tingkah laku penyerapan dengan menggunakan spektrum yang diperolehi dari eksperimen. Dengan itu disyorkan, lebih analisis perlu dilakukan untuk mendapat data yang lebih baik dalam membuat perbandingan setiap sistem.

PROCESS MONITORING OF CO_2 ABSORPTION IN DIETHANOLAMINE USING FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

ABSTRACT

The research is about the process monitoring of carbon dioxide (CO_2) absorption in alkanolamine aqueous solution, Diethanolamine (DEA) by Fourier Transform Infrared Spectroscopy (FTIR). The CO_2 gas level in the atmosphere is rising fast because of the human activities and industry process. It is important to capture CO_2 gas from the flue gas to reduce the emission of gasses in atmosphere. Today, absorption of CO_2 by various alkanolamine solutions is the dominant industrial process for solving the increasing of greenhouse gas emission. In this study, DEA is use as an absorbent in absorption of CO_2. The first objective of the study is to obtain the FTIR spectrum of CO_2-DEA system at different DEA concentration and CO_2 flow rate. The concentrations of DEA are 2M, 4M and 6M. The CO_2 flow rate is 100 and 200 ml/min. The experiment was performed at the constant stirrer speed, 120rpm. The second objective of the study is to synthesize FTIR spectrum to characterize the system using Principal Component Analysis (PCA). The experiment were be conducted by taking the sample for every 1h, 2h, 3h, 4h, 5h, 6h and 7h after CO_2 addition in DEA solution. The samples were analyzed using FTIR. As the conclusion, FTIR spectra for CO_2-DEA system are successfully obtained. FTIR are feasible to be used to monitor the absorption process of CO_2 in different DEA concentration and CO_2 flowrate because it gives a fast analysis and reliable measurement. The multivariate technique of Principal Component Analysis (PCA) can be applied to characterize the absorption behavior by resulting the spectrum obtained from the experiment. As the recommendation, the more analysis should be done to have better data in making comparison of each system. Besides that, the other variable also can be observed like temperature and pressure. The other amine also can be used as an absorbent like AMP and blending of MDEA with DEA.

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CHAPTER 1

INTRODUCTION

This chapter provide the general ideas on the subject that are going to be study including background of proposed study, problem statement, research objectives, scope of proposed study, expected outcome and significance of proposed study.

1.1 Research Background

Carbon dioxide (CO_2) is the most abundant gas contained in the atmosphere. The amount of CO_2 released in the atmosphere is increasing day by day due to the human activity which is burning the fossil fuels, producing cement, combustion activities and gas flaring in the industry (Chiari and Zecca, 2011). The scenario of the CO_2 emissions level is shown in Figure 1.1 which is the CO_2 emission is getting higher on 2050 if there is no action taken. The carbon dioxide removal from the atmosphere that cause by the consumption of large amount of fossil fuels has become one of the most serious environmental problems which is now being paid attention by public

authorities worldwide (Delgado et al., 2009). According to Wang et al., (2003), 80% of the world total primary energy sources and 60% of the world electricity was supplied by the fossil fuels but the burning of fossil fuels itself in industry is the main contribution to the increment of CO_2 emission which is the most important. As stated by Fernandes et al., (2012), the power generation from the fossil fuels, estimated for approximately 25% of global CO_2 emission and this are set to increase dramatically over the next 25 years. The coal-fired power plant produces and released CO_2 to the atmosphere, a major greenhouse gas. The greenhouses gasses will bring to the environmental global climate change. As stated by Thitakamol et al,. (2007), the coal combustion could contribute approximately 41% of the total world CO_2 emissions (43,676 million metric tonnes of CO_2) in 2030. It is important to capture CO_2 gas from the flue gas to reduce the emission of gasses in atmosphere. Today, absorption of CO_2 by various alkanolamine solution is the dominant industrial process for solving the increasing of greenhouse gas emission (Sulaiman et al., 1998). Monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) is the commonly three type of alkanolamine were used in the industry as an absorbent in removal of CO_2. In this study, DEA is used as an absorbent in the analysis due to the advantages to remove CO_2 gas. The absorption of the CO_2 in DEA solution will be analysed using Fourier Transform Infrared Spectroscopy (FTIR).

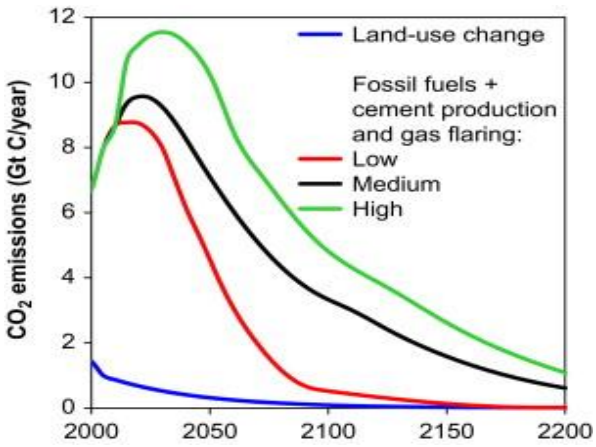

Figure 1.1 Anthropogenic CO_2 emissions from fossil fuels, cement production, gas flaring and land-use changes: the present Low, Medium and High scenarios are shown

(Sources: Chiari and Zecca, 2011).

1.2 Problem Statement

Increase in CO_2 gas emission in atmosphere was brought to the global environmental problem which is increase in greenhouse gases. According to UNEP (2005), global concentrations of CO_2 in the atmosphere have increased from pre-industrialisation levels of approximately 280 parts per million by volume (ppmv) to approximately 316 ppmv in 1958 and rapidly increased to approximately 369 ppmv today. Global CO_2 concentration is estimated to increase above 750 ppmv by 2100 if there is no action is taken to solve the current situation. According to Freund, (2003), power generation from fossil fuel fired-plant which is coal and natural gas is one of the main sources of CO_2 emission. However, the fossil fuel-fired plant plays an important role in supply the energy and electricity to the world. The fossil fuel fired-

plant should be operated flexibly in fulfil the all demand from the world. The increasing of the atmospheric concentration of greenhouse gases, the effective CO_2 emission strategies which are CO_2 capture are required to solve the problem. The CO_2 absorption is well suited for CO_2 capture in industry.

Gas treating using alkanolamines has been practiced in industry for over half a century. However, the method that we have for analysing CO_2 gas concentration is not sufficient and not achieves the good measurement. According to Vogt et al,. (2011), an effective solvent analysis which is considered the characteristic parameters such as the actual loading of solvent during absorption and regeneration is necessary. Today in petroleum industry, a continuous control of the capture efficiency was performed through a balance of gaseous phase by observing the CO_2 concentration in raw and cleaned gas which is this technique is not effective. Furthermore the operator also need to apply the empirical knowledge by enhancing the solvent flow ratio, application of additives, partial exchanges of the solvent or elevating the regenerator temperature and this all action will caused the higher operation cost and a long of time is needed in identified the main cause of the inefficiency of the CO_2 capture in order to optimized the process. From the problem that had faced by the industry, a new fast and effective absorption measurement is needed in obtaining the accurate and effective result.

The method based on infrared ray absorption has been found to passes the wide measuring range and fast response. In this study, the experimental of CO_2 absorption in DEA solution will be measured using FTIR which is the fast analysis. By investigate the FTIR spectrum of CO_2-DEA system at different process variables

by produces a molecular fingerprint of the sample with absorption peaks, industry will have a reference from data of the system for making the predictive models without time consuming.

1.3 Research Objectives

The objectives of this study are:

1.3.1 To obtain the FTIR spectrum of CO_2-DEA system at different process variables which is amine concentration and CO_2 gas flow rate.

1.3.2 To synthesize FTIR spectrum to characterize the system.

1.4 Research Questions/Hypothesis

1.4.1 What is the measurement of CO_2 absorption obtaining at different process variables using FTIR analysis?

1.4.2 How the system is characterised by using FTIR spectrum?

1.5 Scope of Proposed Study

This study provides a state of the art of the research work carried out in CO_2 capture with chemical absorption. The first scope of the proposed study is to perform the experiment of CO_2 gas absorption in alkanolamine solution which is DEA. The experiment will be run at atmospheric pressure, 1 atm, at room temperature, 25^oC and at different process variables which is the concentration of DEA and CO_2 flow rate. The concentrations of DEA are 2, 4 and 6M and the CO_2 flow rate are 100 and 200 ml/min. The experiment will be performed at constant stirrer speed which is 120 rpm. Then, the amine solution, DEA will be analyzed to CO_2 using FTIR which is a fast analysis instrument and more sensitive than any older dispersive instrument. The characterization will be done by using multivariate method of Principal Component Analysis (PCA).

1.6 Expected Outcome

The absorption of CO_2 in DEA solution, a secondary amine is able to be detected using FTIR which is fast analysis, high sensitivity and good selectivity. The FTIR spectrum of CO_2-DEA system will able to be obtained at different process variables which is at different DEA concentration and CO_2 gas flow rate which will be used in characterized the system. The chemical absorption process occurred during the absorption of CO_2 in DEA solution. Then, PCA is feasible to characterize the system based on the data obtained from the CO_2-DEA spectrum in the experiment that represents the molecular absorption and transmission, creating a molecular

fingerprint of the sample with absorption peaks. The data analysis obtain will able to be used in the processing control, chemical analysis, laboratory analysis and system control application.

1.7 Significance of Proposed Study

Study the process monitoring of CO_2 absorption using DEA by FTIR will bring the benefits towards environment and industry. According to Kierzkowska-Pawlak and Chacuk (2010), the absorption of CO_2 from flue gas will reduces the emission of greenhouse gasses, which is the solution of the alkanolamine, DEA play an important role in capture the CO_2 gas. Global warming is caused by emission of greenhouse gases which is 72% of the totally emitted greenhouse gases is CO_2. By CO_2 capture in reducing the CO_2 emission will result in minimizing the climate change. Besides that, by action taking to decrease CO_2 concentration in atmosphere will reduce the potential burdens to human health.

FTIR spectrum of CO_2-DEA system at different process variables which is DEA concentration and CO_2 gas flow rate will be obtained using FTIR as to detect CO_2 in DEA solution. Jackson et al., (2009) state that FTIR brought the faster analysis of chemical analysis to be carried out. CO_2 can be detected very fast using FTIR with the method based on radiation. The FTIR spectrum is synthesize to characterize the system using PCA. Besides that, process monitoring of CO_2 absorption using DEA by FTIR will give the benefit towards industry which is based on the result obtain in the experiment, it can be used in industry as a reference to

capture the CO_2 in reducing the emission of CO_2 in the atmosphere that produced by the industry activity and also can be used in control system application (Zhang and Wu, 2004).

1.8 Concluding remarks

The chapter already review the introduction of absorption of CO_2 by using alkanolamine which is DEA solution. It also reviewed about the scope and the significance of the study. The next chapter will discuss more about the literature and theoretical of the research about the absorption of CO_2, the reaction mechanism, the analysis of CO_2 detection, FTIR, the type of alkanolamine that used as an absorbent and review of PCA.

CHAPTER 2

LITERATURE REVIEW

This chapter provide the general ideals on the subject that are going to be study including introduction, absorption principle which is physical and chemical absorption, reaction mechanism of CO_2 absorption in DEA, Fourier Transform Infrared Spectroscopy (FTIR) Analysis, Principal Component Analysis (PCA) and the type of absorbent.

2.1 Introduction

The CO_2 gas level in the atmosphere is rising fast because of the human activities and industry process. Increases in amounts of greenhouse gases and other harmful gases into the atmosphere are caused by the fossil fuel usage (Chiari and Zecca, 2011). Scientist realized that a gas in the atmosphere is the main cause of the greenhouse effect which brought to the effects of earth's temperature. The greenhouse effect refers to the phenomenon whereas the gases in the upper

atmosphere absorb a portion of the heat radiated by the earth. The earth's temperature is estimated in range of 33^{o}C warmer than it would be if this energy were instead transmitted to space (Cooper and Alley, 1994). Absorption into liquid solvents, adsorption on solids, cryogenic capture and permeating via membrane are the examples of the separation technologies that are available for the removal of CO_2 gas nowadays but absorption is most efficient based on the researcher's opinion (Ajibola, 2010). According to Lawal at al., (2011), there are two type of absorption include in the separation technologies for CO_2 removal which is physical and chemical absorption. As discussed by Jamal and Meisen, (2001), this type of absorption is the dominant industrial process for the separation of acid gases such as CO_2 and H_2S, from mixtures in natural gas processing. DEA is the secondary type of amine which is popular commercially used absorbent. Principal component analysis (PCA) will be used to characterise the system which is generally considered to be the working horse of multivariate data analysis.

2.2 CO_2 Absorption/Desorption In Aqueous Amine

Amine-based CO_2 capture has been widely considered as a feasible ideal technology for reducing large-scale CO_2 emissions and mitigating global warming (Zhou et al., 2011). Sholeh et al., (2007) stated that the amine-based CO_2 capture process has become a common method for CO_2 removal because it is energy efficient which is in the amine-based CO_2 capture process, an amine solvent is used to absorb CO_2 from the flue gas, and CO_2 is subsequently extracted from the amine solvent, which can then be regenerated and reused. CO_2 capture using aqueous amine is a well-